

FINAL REPORT
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Waste Volume Reduction Using Surface Characterization and Decontamination by
Laser Ablation

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Executive Summary

Laser ablation was studied as a method for removing contaminated surface layers from concrete. The objectives of this research were to determine the mechanism and efficacy of laser ablation, to understand the chemistry of contaminated concrete surfaces, and to chemically and physically characterize the captured ablation effluent. Laser ablation is attractive because it produces the smallest possible waste stream, offers fine control over the amount of material removed, can work on cracked, curved or irregular surfaces, and can potentially be instrumented for real-time analysis. While the focus of this project was on concrete, the information should be applicable to any surface requiring contaminant removal. The intent is to learn how to use lasers as tools to do various decontamination jobs.

The study proceeded on two parallel tracks, fundamental studies of high power ablation, and chemical characterization of the concrete and effluent. Our ablation work has shown that a pulsed laser ablation system is scalable and robust. Removal rates can be predicted for lasers of arbitrary power. Ablation efficiency can be maintained over a wide range of conditions. Material can be removed to any desired depth, and focus and working distances can be adjusted to adapt to corners, cracks, or weathered or irregular surfaces. When used properly, laser ablation produces an effluent consisting primarily of small chunks of material, up to about one millimeter in size, that are not thermally processed by the laser and have essentially the same chemistry as the original surface. The process also produces a small amount of aerosol, which can be chemically distinct from the original concrete and may represent a health hazard. Poor choice of ablation parameters can result in larger amounts of aerosol and therefore worse

hazards. Decontamination technologies based on laser ablation require fundamental studies such as these in order to insure that systems are chosen and used properly.

The studies on chemical speciation showed that cesium is very loosely bound in concrete, and therefore volatile. Technologies such as microwave heating or laser ablation that heat radioactive cesium-contaminated concrete must take cesium volatility in account. Likewise, aerosol particles produced by ablation showed segregation of cesium and strontium into particles of differing sizes. These particles will become stored waste, and thus decontamination technologies that produce aerosols must take into account that fact that the particles may have very different chemical composition than the original material, depending on the nature and extent of heating.

Research Objectives

The U.S. Department of Energy's nuclear complex, a nation-wide system of facilities for research and production of nuclear materials and weapons, contains large amounts of radioactively contaminated concrete[1]. This material must be disposed of prior to the decommissioning of the various sites. Often the radioactive contaminants in concrete occupy only the surface and near-surface (~3-6 mm deep) regions of the material. Since many of the structures such as walls and floors are 30 cm or more thick, it makes environmental and economic sense to try to remove and store only the thin contaminated layer rather than to treat the entire structure as waste. Current mechanical removal methods, known as scabbling, are slow and labor intensive, suffer from dust control problems, and expose workers to radiation fields. Improved removal methods are thus in demand[2-5].

Prior to decontamination, the surface must be characterized to determine the types and amounts of contaminants present in order to decide on an appropriate cleaning strategy. Contamination occurs via exposure to air and water-borne radionuclides and by neutron activation. The radionuclides of greatest concern are (in order of abundance) [1]: ^{137}Cs & ^{134}Cs , ^{238}U , ^{60}Co , and ^{90}Sr , followed by ^3H , radioactive iodine, and a variety of Eu isotopes and transuranics. A system capable of on-line analysis is valuable since operators can determine the type of contaminants in real time and make more efficient use of costly sampling and characterization techniques. Likewise, the removed waste itself must be analyzed to insure that proper storage and monitoring techniques are used.

The chemical speciation of radionuclides in concrete is largely unknown. Concrete is a complex material comprising many distinct chemical and physical phases on a variety of size scales[6-8]. Most studies of radionuclides in cements and concrete are for the most part restricted to phenomenological treatments of diffusion of ions, particularly Cs, in and out of model waste forms and engineered barriers[9-21]. Few studies exist on the chemical speciation of the contaminants themselves in concrete [22-25]. For example, the extent to which various contaminants react with the cement and various aggregate particles is currently unknown, as is the role of the high pH of the cement pore water on ion partitioning and chemical speciation. DOE has designated understanding the chemical nature of the contaminants as important in the rational design of characterization, decontamination, and waste handling strategies[26, 27].

We have investigated laser ablation as a means of concrete surface removal[28-31]. Lasers are attractive since the power can be delivered remotely via articulated mirrors or fiber optic cables and the ablation head can be manipulated by robots, thus avoiding exposing workers and the laser system to the radiation field. In addition, lasers can be instrumented with spectrometers or effluent sampling devices to provide for on-line analysis. In contrast to mechanical scabbling systems, laser beams can penetrate cracks or follow very rough or irregularly shaped surfaces. Finally, a laser ablation system produces the smallest possible waste stream since no cleaning agents such as detergents or grit (from grit blasting systems) are mixed with the effluent.

Industrial multi-kilowatt Nd:YAG and CO_2 lasers are capable of ablating concrete surfaces and effecting decontamination. Both continuous wave[32-36] and pulsed[28-31, 35] systems have

been investigated, with the main difference lying in the mechanism of ablation. Pulsed systems rely on the thermal shock produced in a small volume of rapidly heated material to disaggregate and explosively remove concrete[33-36], while cw lasers either melt the surface[36] or rely on the differential thermal expansion of the various components of concrete (i.e. cement, sand, and aggregate) to induce thermal stress in a large volume, which results in the fracture and removal of material[33, 34]. Continuous wave systems are sensitive to changes in the laser focus and the water content of the concrete, and have a maximum removal depth of about 8 mm[33, 37].

Our work has shown that a pulsed Nd:YAG ablation system is scalable, so that removal rates can be predicted for lasers of arbitrary power, and maintains ablation efficiency over a wide range of conditions, making for an inherently robust system. Material can be removed to any desired depth, and focus and working distances can be adjusted to adapt to corners, cracks, or weathered or irregular surfaces. In addition this work has increased the body of knowledge on cesium and strontium speciation in concrete, and has delineated the effects of ablation parameters on the final disposition of these species in the ablation effluent. Decontamination technologies based on laser ablation require fundamental studies such as these in order to insure that systems are chosen and used properly.

Methods and Results

Concrete surfaces were ablated with an industrial 1600 W pulsed Nd:YAG laser operating at its fundamental wavelength of 1064 nm, as shown in Figure 1. The beam was delivered via a 10 m long by 1 mm diameter fiber optic cable and focused on the surface to spot sizes ranging from 0.5 mm to a few mm in diameter. The laser itself is not shown in the figure. The fiber optic cable carrying the beam enters the focusing head from just off the top of the picture. The laser pulses were 0.5 to 2 ms in duration depending on the operating parameters. The laser pulse repetition rate was variable up to 800 Hz, with a maximum duty cycle of 40%. The computer-controlled sample stage was moved in three dimensions under the stationary beam focusing head. A seven-stage particle impactor (horizontal metal cylinder at left in Figure 1) was used to collect and analyze the size distribution of the aerosol portion of the ablation effluent. Ablation efficiency, removal depths, and removal rates were determined as functions of irradiance, pulse overlap, and focal position, as well as other parameters. The virgin and ablated surfaces and ablation effluent were chemically and physically characterized with electron microscopy, energy dispersive X-ray spectroscopy, mass spectrometry, and neutron activation analysis to determine contamination routes and ablation mechanisms, and to optimize the process. In addition, optical emission spectra of the ablation plume were obtained on-line during the laser ablation process itself.

Figure 2 shows a laser ablation track in high density concrete. The laser made twenty passes across the surface, ablating a 1 mm wide by 3 mm deep track on each pass. Deeper tracks could be made by either slowing the laser raster rate, or making multiple passes over the same track. The merits of each approach are discussed below.

Our work has shown that several different material removal mechanisms exist simultaneously when concrete is irradiated at high power with a pulsed laser[28-31]. The most important is the thermal shock created by the laser pulse. Since concrete is a thermal insulator, the rapid heating induced by the millisecond laser pulse is adiabatic to first order. Thermal expansion causes

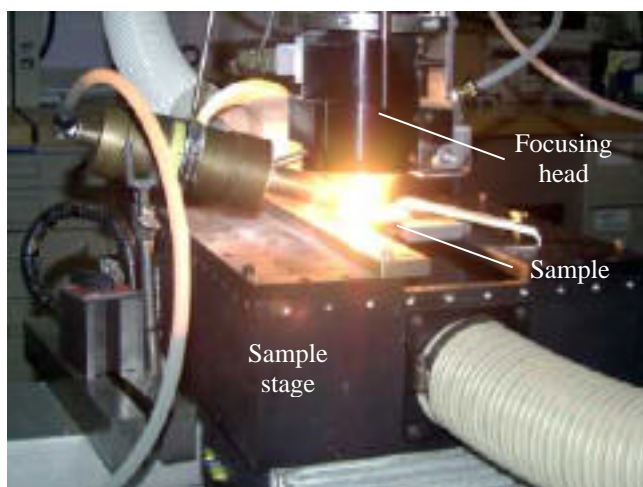


Figure 1: 1600 W pulsed Nd:YAG laser ablation system in operation, showing the bright plume of hot gases generated by the process.



Figure 2: Laser ablation track in high density concrete. The track is twenty mm wide by 3 mm deep, and results from twenty passes of the laser, each ablating a 1 mm wide groove.

stress to build up at the interface between the plug of laser-heated material and the cold surrounding bulk. When the induced stress exceeds the tensile strength of the material, the concrete fractures into small pieces, ranging from a few microns to a few millimeters in diameter, which explode off the surface. Figure 3 is an optical micrograph of the effluent produced by the thermal shock mechanism. The process is efficient since most of the material is not heated to its melting or vaporization temperature. Because the thermal shock mechanism dominates, it largely controls the overall material removal rate. Material is not heated to high enough temperatures or for sufficient periods of time for contaminants to migrate, so the bulk of the effluent is not significantly different chemically from the original material.

The ablation rate was found to depend on several factors. The most important were laser power, pulse overlap rate, and focal position with respect to the surface. In general, high power, fast raster rates and large beam diameters lead to the highest removal rates. The ablation efficiency, defined as mass removed per unit energy delivered to the surface, is unaffected by parameters such as total power or focused spot size. In particular, the ablation efficiency is constant at 0.23 mg/J over a wide range of irradiance values (power per unit area). Figure 4 is a plot of efficiency vs. irradiance obtained on a sample consisting of 40% Type I Portland cement and 60% sand. (Sample preparation details are given elsewhere[29,30]. This finding is important for two reasons. First, it shows that ablation with a pulsed laser is inherently robust, since power fluctuations or variations in focus - both of which affect irradiance - do not affect efficiency. The removal efficiency of concrete with continuous wave lasers is critically sensitive to irradiance, and therefore more difficult to control and extrapolate from one laser system to another[33, 34, 36]. Second, it shows that the pulsed laser process is scalable to lasers of arbitrary power, since the laser spot size can always be easily adjusted to keep the irradiance within the wide bounds determined by this study. Thus when done properly, the ablation rate scales only with the total laser power. This finding makes it possible to predict ablation rates for any Nd:YAG laser system with pulse lengths similar to those used in our study, i.e. 0.5 to 2 ms.

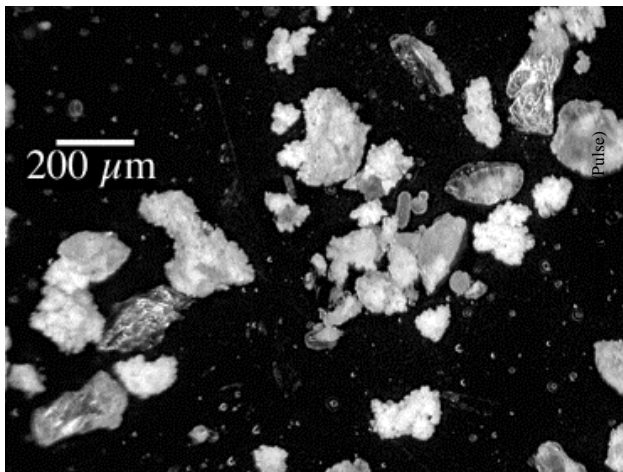


Figure 3: Optical micrograph of the major portion of the ablation effluent from concrete. The grainy particles are disaggregated cement, the smoother ones are fractured sand grains.

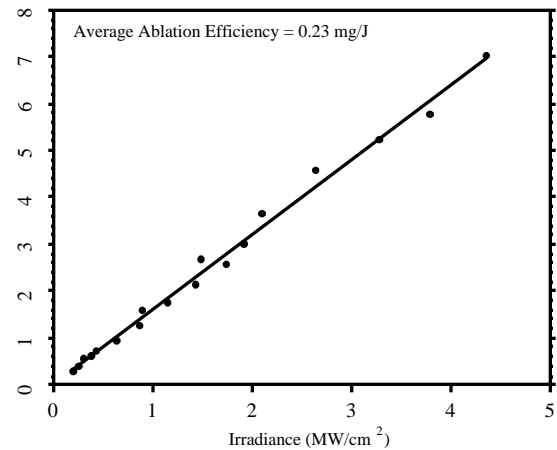


Figure 4: Concrete removal rate as a function of laser irradiance. The straight line fit gives (with appropriate unit conversion) the process efficiency.

We have found that efficiency drops at slow raster rates where consecutive pulses overlap significantly. Pulse overlap occurs when a given laser pulse irradiates a region of the surface that was irradiated during the previous pulse. As a simple example, if the laser spot diameter is 1 mm and the sample moves 0.5 mm between pulses, then the linear pulse overlap is 50%. (In practice the calculation is slightly more complicated since the sample is also moving during the pulse, so that the irradiated area is an oval rather than a circle.) At overlaps between 0 and 50% some regions of the surface receive two consecutive pulses. When linear overlap exceeds 50%, some regions receive three or more consecutive pulses.

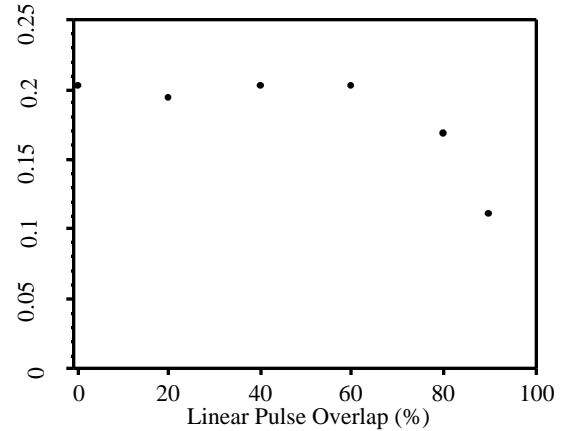


Figure 5: Concrete ablation efficiency as a function of pulse overlap.

Figure 5 shows the effect of pulse overlap on ablation efficiency. Efficiency is constant at about 0.2 mg/J up to 60% overlap. Average surface exposure (total energy delivered per unit area) increases as overlap increases, resulting in deeper ablation grooves and no loss of efficiency up to 60% overlap. As overlap exceeds 60% the efficiency drops, i.e. the increased surface exposure does not result in proportionately increased ablation depth. Photographs of ablated surfaces at various pulse overlaps (Figure 6) show the cause of this behavior, namely that high overlap causes melting rather than ablation of the material. At pulse overlaps up to 50% no portion of the surface receives more than two consecutive pulses, and the ablated surface is grainy and unmelted (Figure 6, left). At 60% the average surface exposure is 2.3 pulses. The ablation grooves are deeper and some slight melting is noted in the rounding of the edges (Figure 6, center), though no drop in ablation efficiency is seen. At overlaps greater than 60% a great deal of melting is seen (Figure 6, right). When three or more consecutive pulses are incident on a given area there is a great deal of residual heat left in the material so that the final temperature after any given pulse exceeds the melting point. Laser energy that would otherwise have been used to remove material via the thermal shock mechanism is instead wasted in the energy-

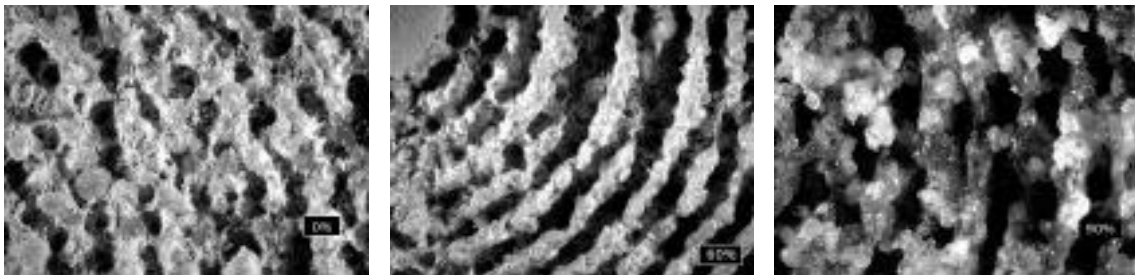


Figure 6: Optical micrographs of ablation tracks in concrete. Left: 0% pulse overlap showing no melting of the substrate. Field of view: 3x4 mm. Center: 60% overlap, showing deeper grooves and some melting. Field of view: 4x5.5 mm. Right: 90% overlap showing significant melting. Field of view: 4x5.5 mm.

intensive phase transition required to melt or even vaporize the cement. The system begins to behave like a continuous wave laser, which glazes the surface as it passes over it[36].

This result quantifies the trade-off between ablation depth and efficiency in a fundamental way, i.e. as dependent on the heat transfer and residual heat left in the material after ablation. In any pulsed laser scenario, concrete will fracture along a surface across which the induced stress exceeds the tensile strength. We have already shown that ablation efficiency is unaffected by wide changes in irradiance, implying that the absolute temperature at that surface at the moment of fracture is constant. Thus for any high duty cycle pulsed system, heat transfer out of the ablated volume is constant over a wide range of conditions. Efficiency drops as the average number of consecutive pulses received by the surface exceeds ~ 2.3 , which corresponds to an overlap of 60% as shown in Figure 5. Average surface exposure is easily calculated from the laser pulse length, repetition rate, and raster rate. This means that one can easily determine the most efficient (cheapest, fastest) way to remove a given depth of material, i.e. whether it is better to make a few deep ablation passes or many shallow ones.

The effluent produced by the ablation process is the material that would become stored waste. The chemical composition of the effluent may or may not be the same as that of the original material depending on the choice of ablation conditions. Under appropriate conditions as outlined above, the vast majority of the effluent consists of chunks of fractures and disaggregated material, i.e. concrete powder, however there is always a small amount of fine aerosol. The amount of aerosol is significantly enhanced as melting increases and efficiency drops. Portland cement comprises only about 10 - 15% of the mass of high density concrete, but it is important because it is the phase, which carries the bulk of the contamination in concrete exposed to water-born radionuclide ions such as Cs and Sr[16], and is the major constituent of the aerosol phase of the effluent.

Figure 7 plots the aerosol particle size distribution obtained from the impactor shown in Figure 1. The distribution is bimodal, with peaks at the high (8.5 μm) and low (<0.5 μm) ends and a minimum at about 1 μm . This suggests that particles form by two mechanisms, namely vaporization / condensation for small particles, and melt/spatter for large particles. This interpretation is bolstered by several lines of evidence. Electron microscopy showed that many of the larger aerosol particles are hollow, suggesting that they formed from molten material. Energy dispersive x-ray (EDX) spectroscopy showed that small particles have disproportionately large concentrations of aluminum compared to both the larger particles and the virgin cement. (Aluminum is present in Portland cement as an aluminate phase[8].) Figure 8 shows EDX spectra of 5 μm and 16 μm aerosol particles. The virgin cement aluminum content was $\sim 2.5\%$, while the 5 and 16 μm particles had aluminum contents of 7.5% and 4.5%, respectively. This suggests that small

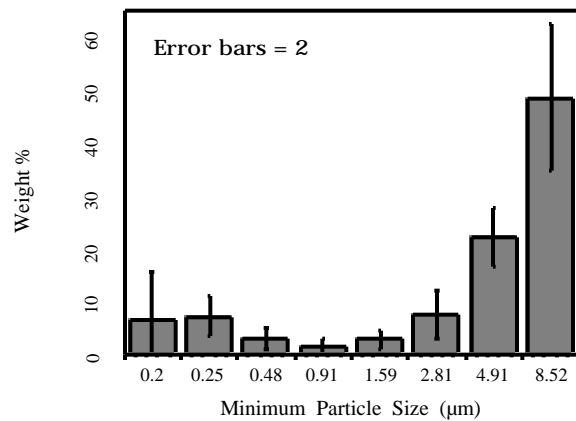


Figure 7: Aerodynamic particle size distribution of the aerosol portion of the concrete ablation effluent.

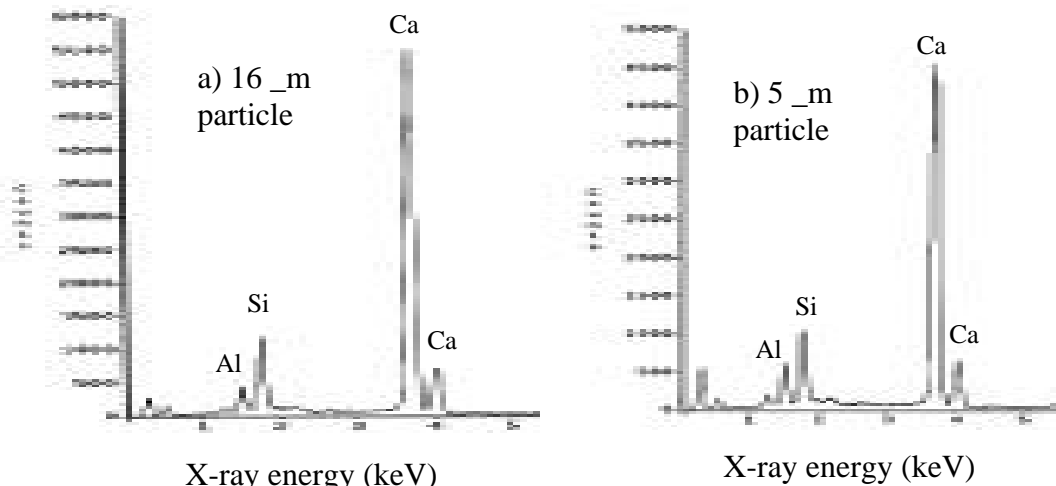


Figure 8: Energy dispersive x-ray spectra of a) 16 μm and b) 5 μm diameter aerosol particles produced by laser ablation of concrete. The smaller particles are enriched in aluminum; the 5 μm particle contains 7.5% aluminum vs. 4.5% for the 16 μm particle. The aluminum content of the virgin cement was $\sim 2.5\%$.

particles form by condensation from vapor, with an aluminum-rich nucleating phase.

Neutron activation analysis (NAA) of aerosol ablated from concrete samples doped with Cs and Sr (1% wt/wt) showed that cesium and strontium concentrations in the aerosol were strongly correlated with particle size, as shown in Figure 9. (Neutron activation analysis was used for this analysis because EDX is not sensitive enough to quantify cesium and strontium in our samples.) Figure 9 shows that particles with aerodynamic diameters below 0.5 μm are enriched in cesium by up to a factor of two compared to the virgin cement, while larger particles are substantially depleted. In contrast, particles in the aerodynamic size range from 0.5 to 1.6 μm were enriched in strontium by up to a factor of two over the virgin cement, while all others were depleted. The horizontal hatched regions in Figure 9 represent the expected amounts of cesium and strontium depending on the degree of dehydration of the aerosol particles.

The NAA data is consistent with the proposed particle formation mechanisms. Since cesium is very volatile compared to the other elements in the cement, it should be distilled out of the melted material

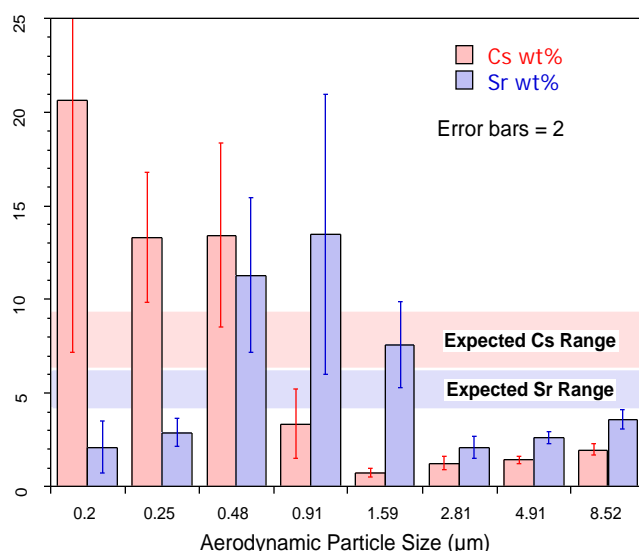


Figure 9: Neutron activation analysis of aerosol particles from laser ablation of concrete, showing segregation of Cs and Sr within the particle size distribution.

and appear in the particles formed from the vapor phase. Also, as previously noted, the small particles tend to be enriched in aluminum, and cesium has been shown to have an enhanced affinity for the aluminate mineral phases found in cement[24]. Strontium is less volatile and tends to remain with the melted/spattered fraction, though the reason for its preferential precipitation in the smaller of the melted particles is unclear. These results are important because they show that a portion of the original concrete is thermally processed by the laser into a chemically distinct material.

Effluent sampling and characterization schemes, especially on-line methods, must take this into account since failure to do so will result in serious errors in the analysis.

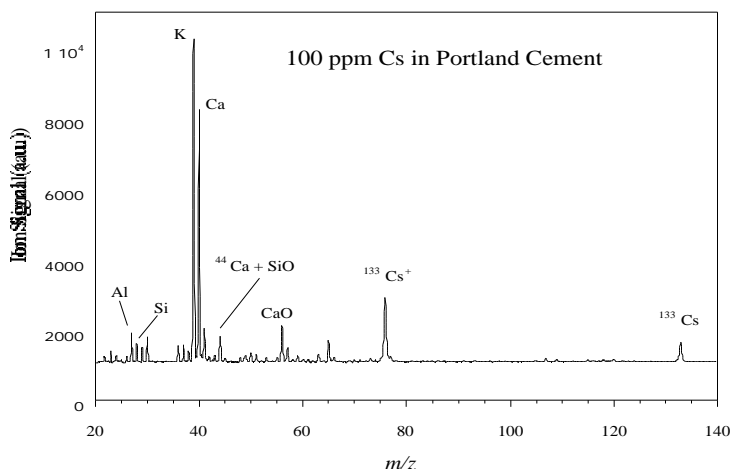


Figure 10: Mass spectrum of ^{133}Cs -doped Portland cement. Desorption wavelength: 338 nm, ionization wavelength: 193 nm. The peak marked $^{133}\text{Cs}^+$ arises from cesium atoms that desorbed as ions rather than neutrals.

Cesium- and strontium-doped Portland cement and high density concrete were also characterized by laser desorption mass spectrometry (LDMS). Small samples, on the order of a few millimeters in diameter, were mounted in a vacuum chamber and pulsed with a low-power laser, typically less than a millijoule per pulse (compared to several joules in the case of the ablation laser). The laser pulse causes atoms to desorb from the surface, and these are ionized by a second laser and analyzed by time-of-flight mass spectrometry. This technique is useful in the present case for analyzing small spots on the surface (down to about one micron) and for providing information about the chemical speciation of the cesium and strontium in the samples.

Figure 10 is a mass spectrum of the surface of a sample of Portland cement doped with 100 ppm cesium-133. The desorption laser wavelength was 337 nm and the ionization laser wavelength was 193 nm. The spectrum shows the especial ease with which cesium is detected by this technique. The major elemental constituents of Portland cement, Ca, Si, and Al are seen, along with K and Cs. Potassium is a constituent of the cement “pore water” and not properly a part of the cement matrix itself[8]. Most atoms desorb nearly exclusively as neutral species and must be ionized by the second laser in order to be mass analyzed. In Figure 10, all peaks except one arise from this process. The peak at an apparent m/z of ~ 72 arises from Cs that desorbed as ions and therefore needed no post-ionization. These moieties are referred to as direct ions, while species that desorb as neutrals and are ionized by the second laser are referred to as photo-ions. For all other species in the spectrum the direct ion to photo-ion ratio is zero, but for Cs it is ~ 3.5 . This reflects cesium’s low ionization potential (3.9 eV).

While Cs direct ions are disproportionately represented due to the low ionization potential, the total Cs signal (direct ions + photo-ions) is also very high considering the small amount of cesium present compared to the other atoms in the material. This is evidence that Cs is very weakly bound to the cement. It is well known that cement contains about 100 times more Ca than K[8], yet the mass spectrum of Figure 10 shows roughly equal amounts of Ca and K. This is because K is a weakly bound, surface-loving species and desorbs far more readily than Ca. Figure 10 suggests that this is also the case for Cs.

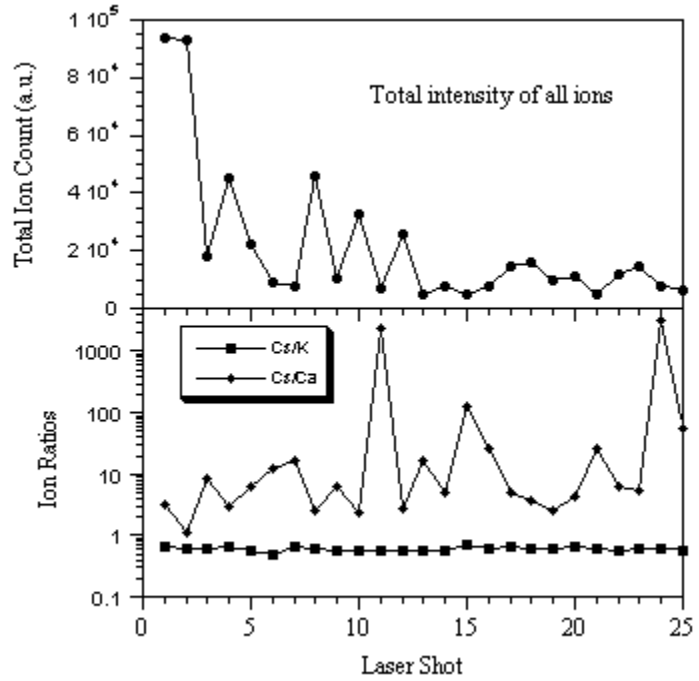


Figure 11: Desorption behavior of Cs, K and Ca from ^{133}Cs -doped cement. Upper panel: total ion intensity as a function of the number laser shots on a given spot. Lower panel: ratios of Cs to K and Cs to Ca, showing the correlation between Cs and K but not between Cs and Ca.

Figure 11 shows an analysis of the desorption behavior of Cs compared to K and Ca. The figure plots the total ions detected (upper panel) and the measured ratios of Cs/K and Cs/Ca (lower panel) over many laser shots. The initial laser shots liberate a great deal of material, primarily the loosely bound species. As the number of shots on a given spot increases, the easily removed material is depleted and the total ion intensity per shot decreases. Ions from later shots represent bulk material and some surface atoms that diffuse into the irradiated area between shots. The lower panel plots the ion ratios over time. Pulse-to-pulse fluctuations in the laser intensity lead to variations in ion intensity that scale with the heat of desorption of the atom of interest. Figure 11 clearly shows that the desorption behavior of Cs correlates strongly with K, while there is no correlation between the Cs and Ca desorption behavior. While the Cs/K ratio varies by less than a factor of 1.5 over all shots, the Cs/Ca ratio varies by a factor of nearly 3000. Table 1 gives a statistical analysis of desorption data for Cs, Sr, K, and Ca. The variance

Sample	Ion	Std. dev. / mean
1	K	0.67
1	Ca	1.22
1	Cs	0.73
2	K	0.22
2	Ca	0.67
2	Sr	0.61

Table 1: Standard deviations as a fraction of the mean of ion signals from cement samples doped with (1) CsCl and (2) SrCl₂. One thousand shots were averaged for each sample. The differences in the values for the same ion ratios across the two samples are due to absolute differences in the desorbing laser intensity.

(standard deviation divided by the mean) of the ion ratios over a series of 1000 laser shots shows that cesium's desorption behavior mimics that of potassium, while strontium's desorption behavior mimics that of calcium. Thus cesium is a pore water constituent like potassium, while strontium has a stronger interaction with the cement and may actually enter the matrix in exchange for calcium. These results help to account for the chemical fractionation observed in the ablation

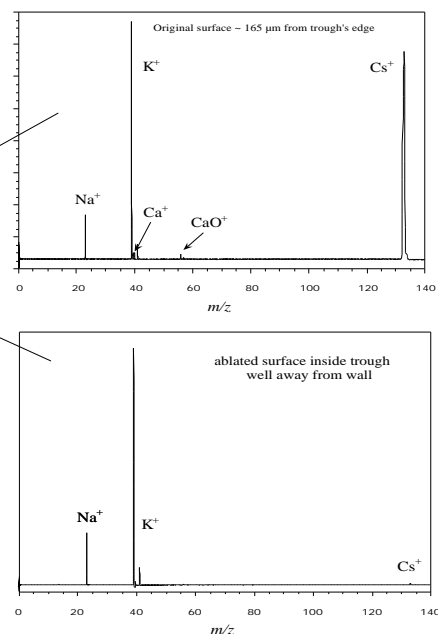
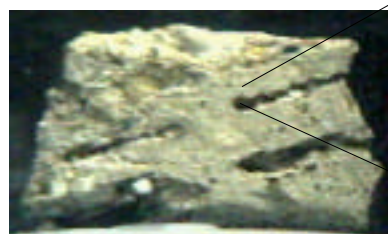


Figure 12: Microprobe laser desorption mass spectra of Cs-doped high density concrete. The upper spectrum shows that the virgin surface contains a large amount of cesium, while the lower spectrum, taken inside the ablation track, shows very little cesium. The ablation track is 1 mm wide and ~0.8 mm deep. The analysis spot size was one micron.

aerosol (Figure 9). Since Cs desorbs much more readily than Sr it should be over-represented in the gaseous portion of the ablation products.

LDMS analysis was also used to establish the efficacy of the decontamination process itself. Figure 12 shows the results of single ablation passes over a sample of high density concrete that had been soaked in a solution of CsCl. The upper mass spectrum shows a lot of cesium on the virgin surface, while the lower spectrum, taken from a one-micron spot inside the 0.8 mm deep track, shows virtually no Cs at all. Thus, Cs is removed with the effluent and is not being driven into the bulk by the laser.

Figure 13 shows optical emission spectra of the ablation plume, i.e. the hot gasses generated during the ablation process as shown in Figure 1. Spectra were acquired from neat, cesium-doped, and strontium-doped samples. In all, 25 calcium, 2 potassium, 2 sodium, 18 strontium and 14 cesium peaks have been identified, all of which originate from relatively low-lying states (less than about $40,000 \text{ cm}^{-1}$) of the neutral species. The fact that the spectra are dominated by low-lying neutral states of the more volatile elements implies that the plasma is relatively cool compared to conventional laser-induced breakdown spectroscopy (LIBS). This is not surprising since the millisecond pulse length of this laser is much longer than nanosecond pulses employed in a typical analytical experiments, resulting in lower peak irradiance and the suppression of multiphoton processes required to produce high-lying states or excited ions. The total LIBS signal correlates with the amount of material removed, so that the technique can be used as a diagnostic tool for the ablation process.

This class of laser has several advantages over traditional LIBS systems. First, the total energy delivered is large, so that each pulse removes milligrams of material compared to nanograms for conventional systems, thus providing a much greater amount of analyte. Second, this class of laser has millisecond pulse and a duty cycle of 40% compared to a pulse length of a few nanoseconds and 0.001% duty cycle for a common LIBS laser. Thus the laser energy can interact with and heat the ablation plume, thus stabilizing it and extending its analytically useful emission lifetime to a millisecond or more, compared to a few microseconds for conventional

LIBS. These features combine to make the spectra exceptionally easy to acquire, as there is a lot of stable long-lived emission signal coming from the plume. Our system needs no time gating or special emission collection optics, both of which are required for conventional LIBS.

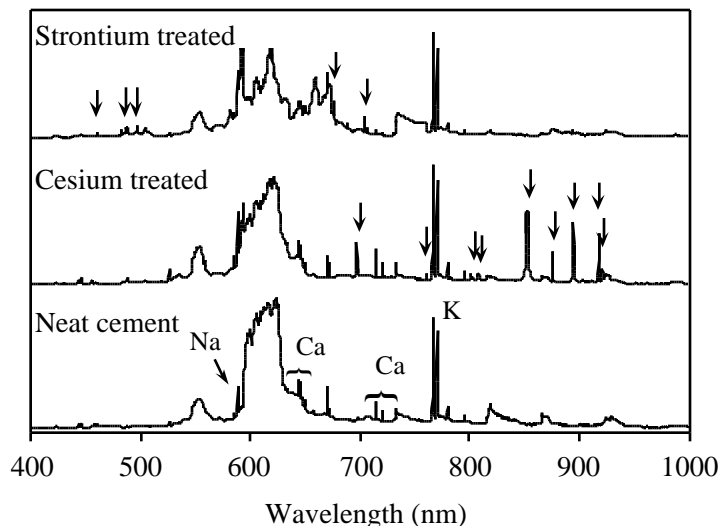


Figure 13: Laser-induced breakdown spectra of the ablation plume from strontium-doped (top), cesium-doped (middle), and neat (bottom) concrete samples. Arrows indicate spectral lines due to the introduced dopants.

Relevance, Impact and Technology Transfer

This work is relevant to DOE's decontamination efforts in the area of surface-contaminated concrete, or other surfaces such as paint or corrosion layers. Lasers can be applied to difficult-to-clean areas such as cracks and corners where other methods are problematic. In addition, the ease with which robots can manipulate a fiber-delivered laser beam makes the technology attractive for areas with very high radiation fields where worker exposure is an issue. There are many kinds of lasers and many parameters controlling laser performance. This study has shown in a systematic way that pulsed lasers can affect surface removal efficiently. Through fundamental studies of the laser-surface interaction this work has shown that to be efficient and to generate the most desirable waste form (i.e. disaggregated concrete) the laser must heat the material rapidly to a temperature at which thermal shock cracks and disaggregates the concrete, but must avoid melting the surface. In practice this is achieved by using a pulsed laser and limiting the residence time of the laser pulse on any given area of the surface by careful control of pulse overlap

Successful deployment of this technology would require little engineering work, since similar low-power systems exist for paint stripping applications. These systems use different lasers, but the fundamentals of delivering the beam and collecting the effluent are the same. This work has provided data to inform decisions on the feasibility of ablation on concrete. In addition, the fundamental work on laser desorption mass spectrometry of Cs-doped surfaces, combined with optical emission spectroscopy of the ablation plume and analysis of the ablation aerosol has shown that Cs volatility is an issue to be dealt with in any decontamination technology that heats the concrete.

Project Productivity

The major project goals as delineated in the original proposal were achieved. The project has met the goal of determining the chemistry of stable isotope analogs of Cs and Sr in concrete. Cesium does not interact strongly with the matrix, but desorbs quite easily, as was shown by both laser desorption profiles and optical emission spectroscopy of the ablation plume. Strontium was shown to behave similarly to calcium in that it did not desorb readily in the mass spectrometry experiments or appear in disproportionate amounts in the ablation plume. A second goal of determining the efficacy of decontamination was met by using laser desorption microprobe analysis to show that laser ablation does not drive cesium into the bulk but removes it with the ablation effluent provided that the laser does not melt the surface. The efficiency of laser ablation was quantified, and parameters for effective removal were determined. A major goal of determining the fate of the contaminants after ablation was also met. The segregation behavior of the introduced cesium and strontium in the ablation effluent was found to be important in its own right from hazard-control standpoint, and was also used to corroborate the chemical speciation studies.

Personnel Supported

The following personnel were supported by or associated with the project:

Michael J. Pellin, Group Leader, Argonne National Laboratory
 Michael R. Savina, Assistant Chemist, Argonne National Laboratory
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Publications

Peer-reviewed journals and books:

“Efficiency of Concrete Removal With a Pulsed Nd:YAG Laser,” Savina, M.R.; Xu, Z.; Wang, Y.; Reed, C.; Pellin, M.J. *Journal of Laser Applications*, **2000**, *12* (5), 200-204.

“Pulsed Laser Ablation of Cement and Concrete,” Savina, M.R.; Xu, Z.; Wang, Y.; Leong, K.; Pellin, M.J. *Journal of Laser Applications*, **1999**, *11* (6), 284-287.

Published in unreviewed publications:

“Laser Ablation Studies of Concrete,” Savina, M.R.; Xu, Z.; Wang, Y.; Reed, C.B.; Pellin, M.J. In *Proceedings of the 18th International Conference on Applications of Lasers and Electro-Optics*, **1999**, Volume 87b, 90-97.

“Laser Ablation of Concrete,” Savina, M.R.; Xu, Z.; Wang, Y.; Leong, K.; Pellin, M.J. In *Proceedings of the 17th International Conference on Applications of Lasers and Electro-Optics*, **1998**, Volume 85a, 219-226.

Interactions

“Concrete Surface Removal and Characterization Using High Power Laser Ablation,” Savina, M.R.; Wang, Y.; Xu, Z.; Reed, C.B.; and Pellin, M.J. Presented at the Environmental Management Science Program National Workshop, Atlanta GA, April 2000

“Laser Ablation Studies of Concrete,” Savina, M.R.; Wang, Y.; Xu, Z.; Reed, C.B.; and Pellin, M.J. Presented at The 18th International Conference on Applications of Lasers and Electro-Optics, San Diego CA, November 1999.

“Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation,” Savina, M.R.; Wang, Y.; Xu, Z.; Reed, C.B.; and Pellin, M.J. Presented at the Environmental

Management Science Program Workshop on Decontamination and Decommissioning, Oak Ridge TN, September 1999

“Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation,” Savina, M.R.; Wang, Y.; Xu, Z.; Reed, C.B.; and Pellin, M.J. Presented at Characterization, Monitoring and Sensing Workshop, Gaithersburg MD, March 1999

“Laser Ablation of Concrete,” Savina, M.R.; Xu, Z.; Wang, Y.; Leong, K.; Pellin, M.J. Presented at The 17th International Conference on Applications of Lasers and Electro-Optics, Orlando FL, November 1998.

“Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation,” Savina, M.R.; Wang, Y.; Xu, Z.; Reed, C.B.; and Pellin, M.J. Presented at The Environmental Management Science Program Workshop, Idaho Falls ID, October 1998

“Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation,” Pellin, M.J.; Savina, M.R.; Leong, K.; Xu, Z. Presented at The Environmental Management Science Program Workshop, Chicago IL, July 1998

Transitions

None.

Patents

None.

Future Work

A proposal for renewal of this project within EMSP was unsuccessful, therefore no future work in this area is planned.

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